Analysis of Bromine-Mercury Reactions in Flue Gas

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Outline

- Objectives
- Introduction - Thermodynamics
- Kinetics and modeling of Hg-Br reactions
- Experimental
  - Homogeneous oxidation by Cl and Br
  - Effects of T profile, NO, Br, reactor surface area
  - Fixed-bed reactor
- Conclusions

Project Objectives

- Develop validated models that allow prediction of extent of reaction between halogens and mercury in coal combustion applications.
- Include homogeneous and heterogeneous reactions.

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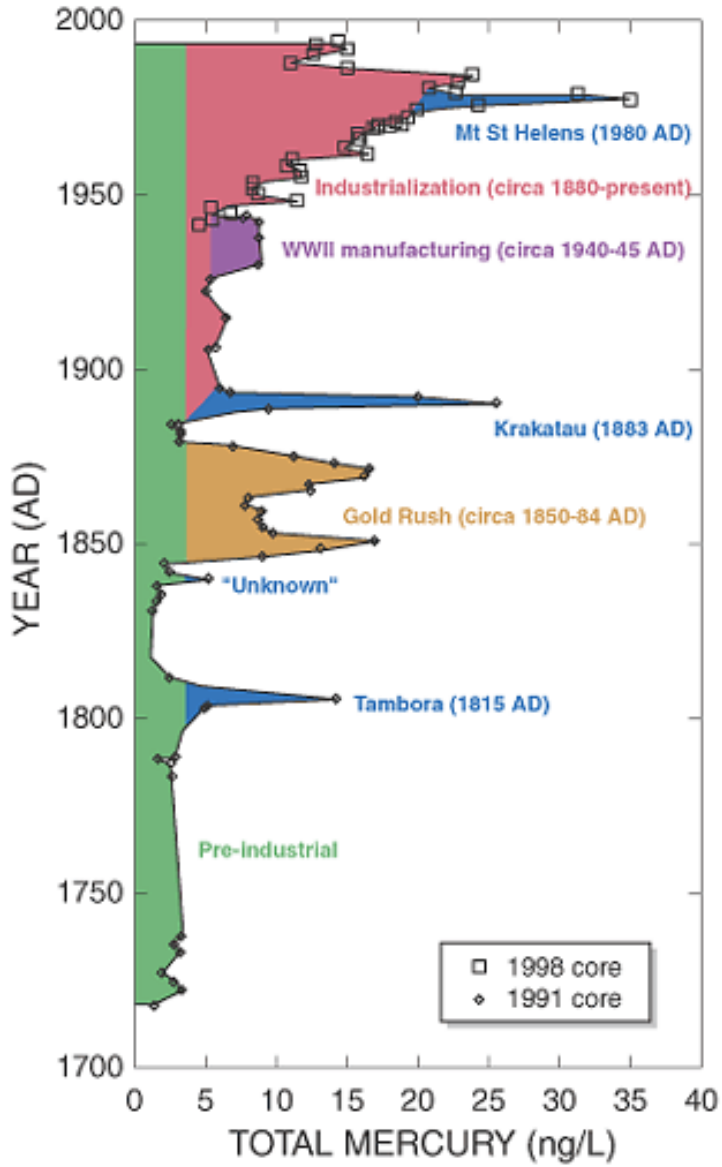
Introduction – Mercury Deposition



Ice core data on total deposited mercury (Wind River Mountains, Wyoming).

http://toxics.usgs.gov/pubs/FS-051-02/

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Introduction - Coal Composition

Sample Description	Elkhor/Hazarc low S bit	**Pittsburgh med S bit**	Illinois 6 high S bit	Wyodak PRB	**Wyodak PRB**	Ohio 5,6,7 high S bit	ND Lignite lignite
ANALYSIS (As Received):							
Carbon	74.87	**76.62**	67.70	53.20	**51.19**	71.07	38.57
Hydrogen	4.59	**4.80**	4.73	4.59	**3.64**	4.81	2.60
Oxygen	8.38	**6.91**	9.19	20.74	**12.29**	8.10	12.52
Nitrogen	1.43	**1.48**	1.18	0.83	**0.72**	1.37	0.42
Sulfur	0.82	**1.64**	3.60	0.22	**0.32**	2.62	0.63
Ash	7.41	**7.01**	10.26	7.36	**6.03**	9.70	9.38
Moisture	2.33	**1.44**	3.31	13.06	**25.81**	2.33	35.88
Total	99.83	**99.89**	99.96	100.00	**100.00**	100.00	100.00
Hg, ug/g	0.13	**0.11**	0.22	0.19	**0.13**	0.15	0.13
Cl, ug/g	1660	**976**	338	**	**26**	974	36
Br, ug/g	25.0	**17.0**	3.7	2.4	**1.2**	23.0	1.9
Cl/Br	66	**57**	91	--	**22**	42	19

Analyses from DOE Toxics program. Equilibrium calculations use Pittsburgh bituminous, 3 % O_2.

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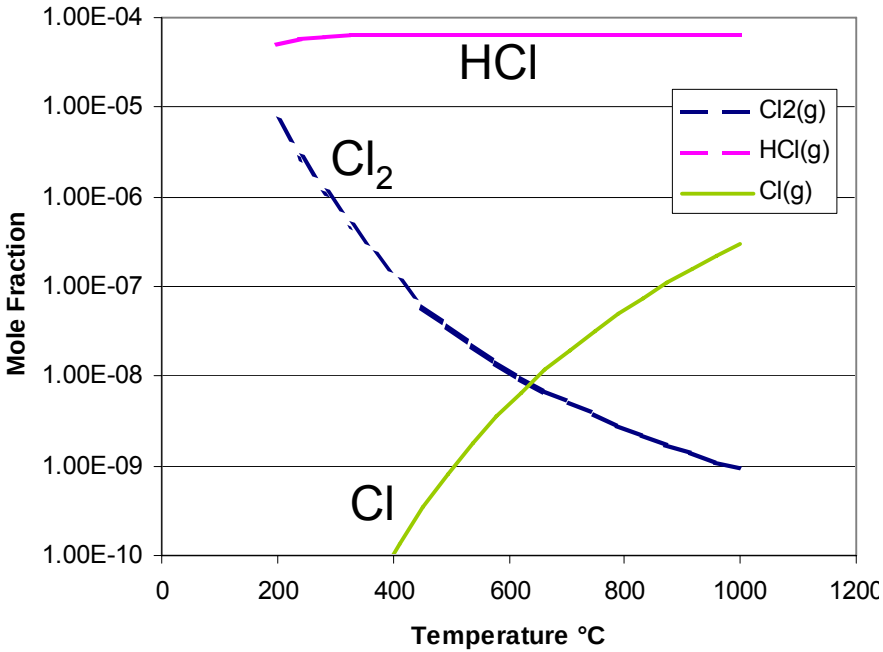
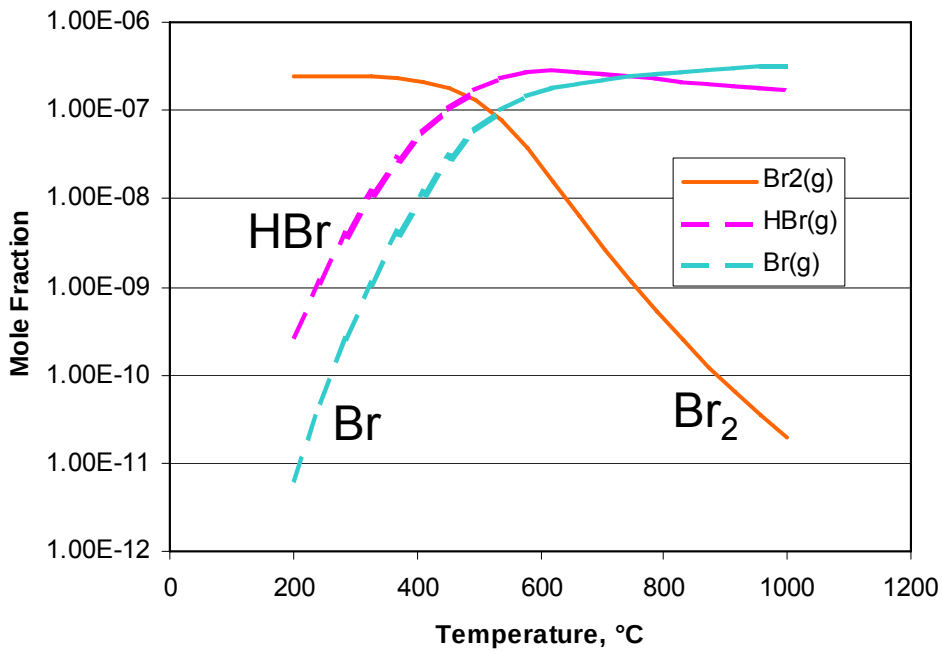
Introduction – Gas-phase Thermodynamics of Cl and Br



HCl is dominant species at all T.



Br_2 is dominant species below 400°C.

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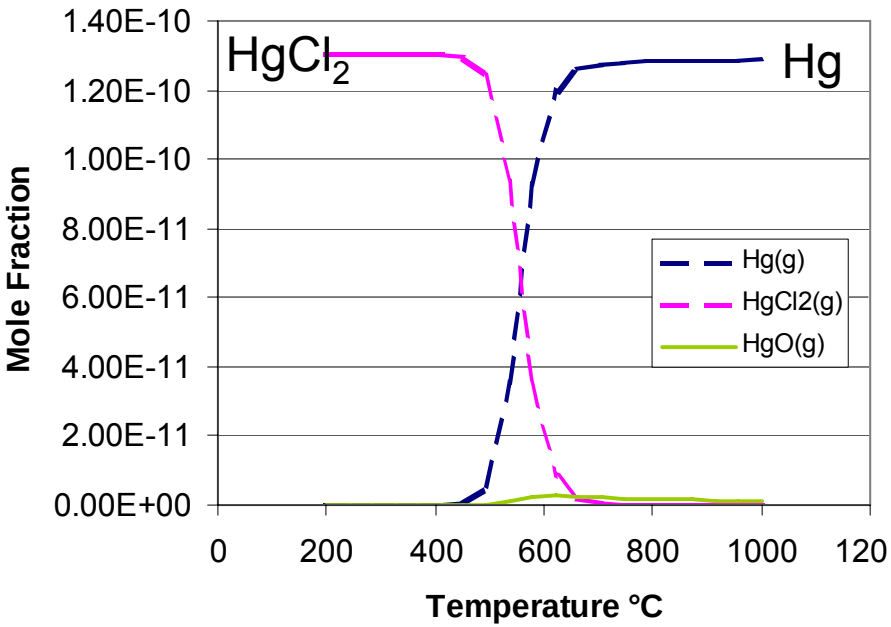
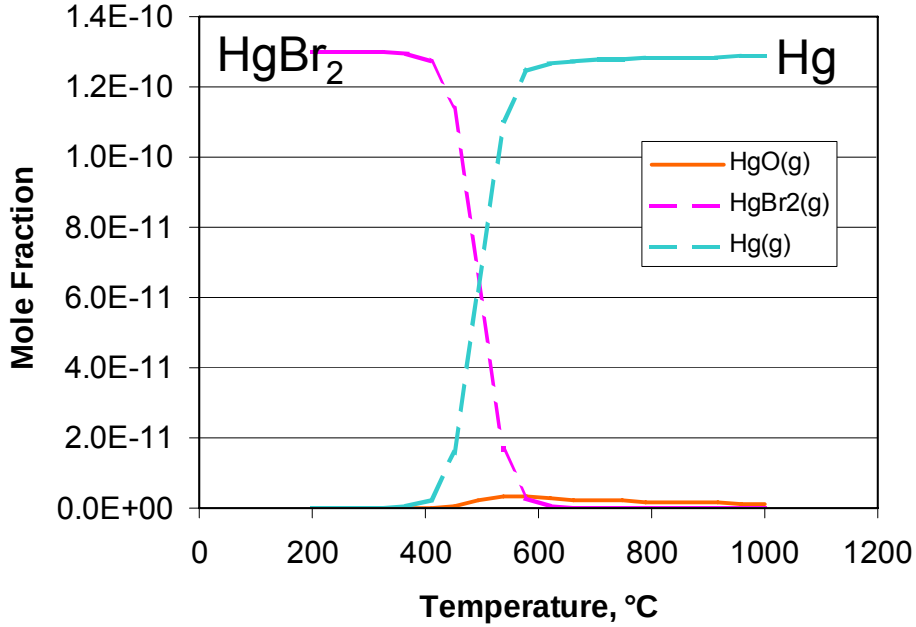
Introduction - Thermo of Hg/Cl, Hg/Br





$HgCl_2$ stable below 550°C.

$HgBr_2$ stable below 500°C. Chlorine excluded from this calculation.

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Kinetics - Hg/Br Reactions

- Theoretical and experimental studies support the following primary homogeneous oxidation pathways

$$Hg + Cl + M \rightarrow HgCl + M$$
$$HgCl + Cl_2 \rightarrow HgCl_2 + Cl$$

$$Hg + Br + M \rightarrow HgBr + M$$
$$HgBr + Br_2 \rightarrow HgBr_2 + Br$$

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Kinetics - Hg/Br reactions

- Bromine-impregnated activated carbon shows 40-80% capture of mercury with hot-side ESP and >90% capture of mercury with cold-side ESP in low-halogen flue gas

Kinetics and Modeling

- Modeling of homogeneous Hg-Cl and Hg-Br reactions
  - 468 reactions, 127 species
  - NO_x, SO_x, Br, Cl chemistry
  - Br chemistry from NIST website
  - Br-Hg chemistry developed for this work
  - 3% excess air, Pittsburgh bituminous

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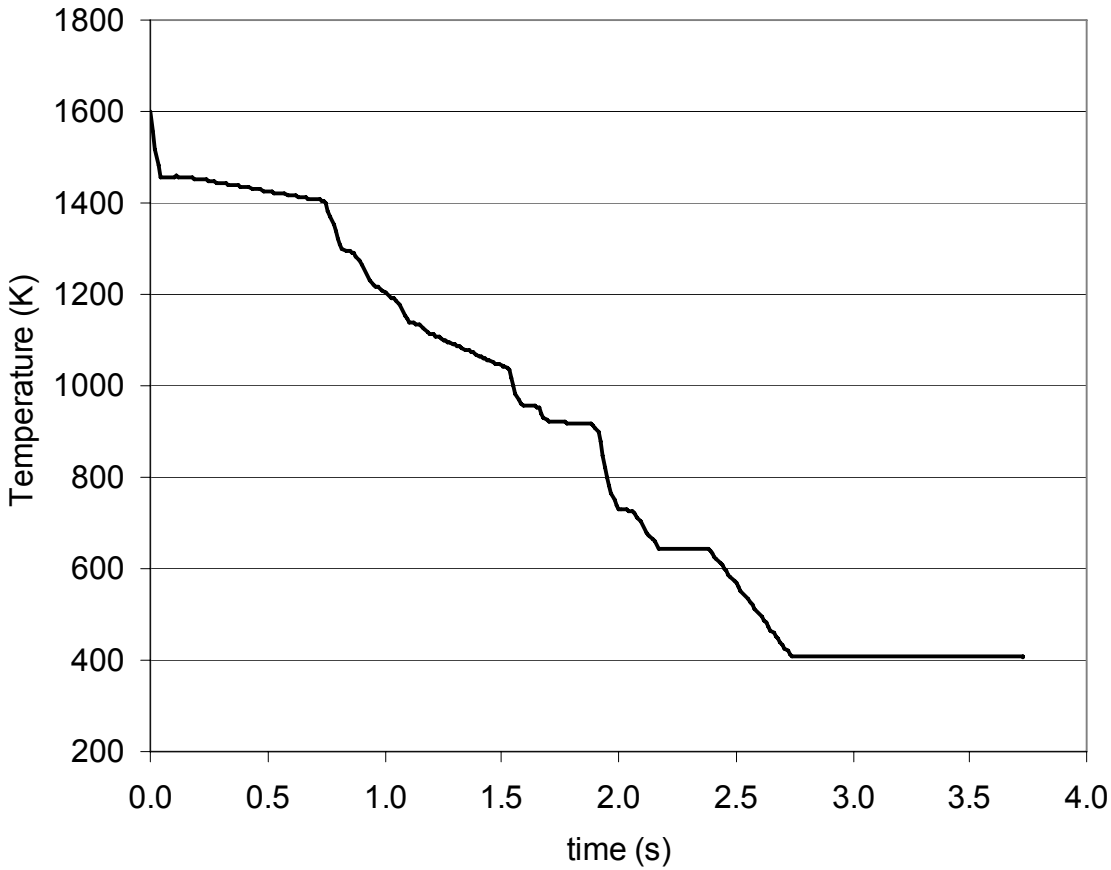
Kinetics and Modeling



Typical time-temperature history in boiler

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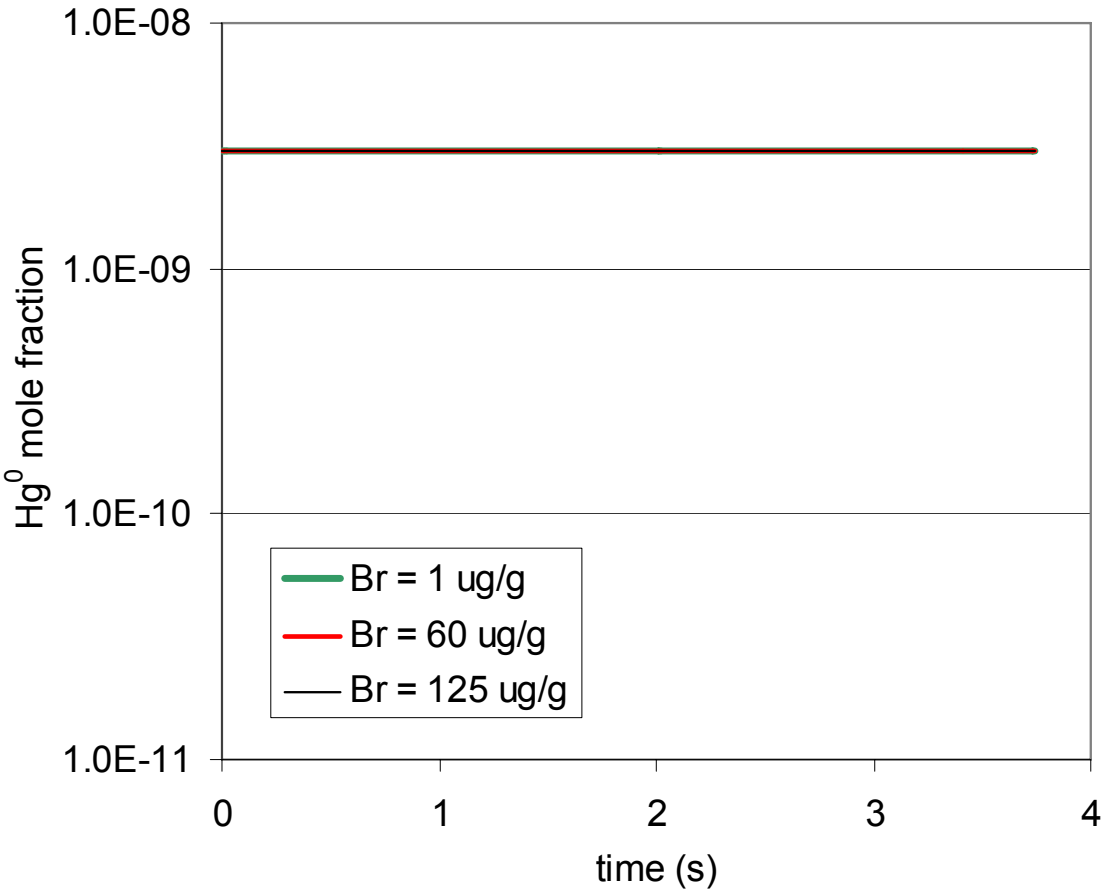
Kinetics and Modeling

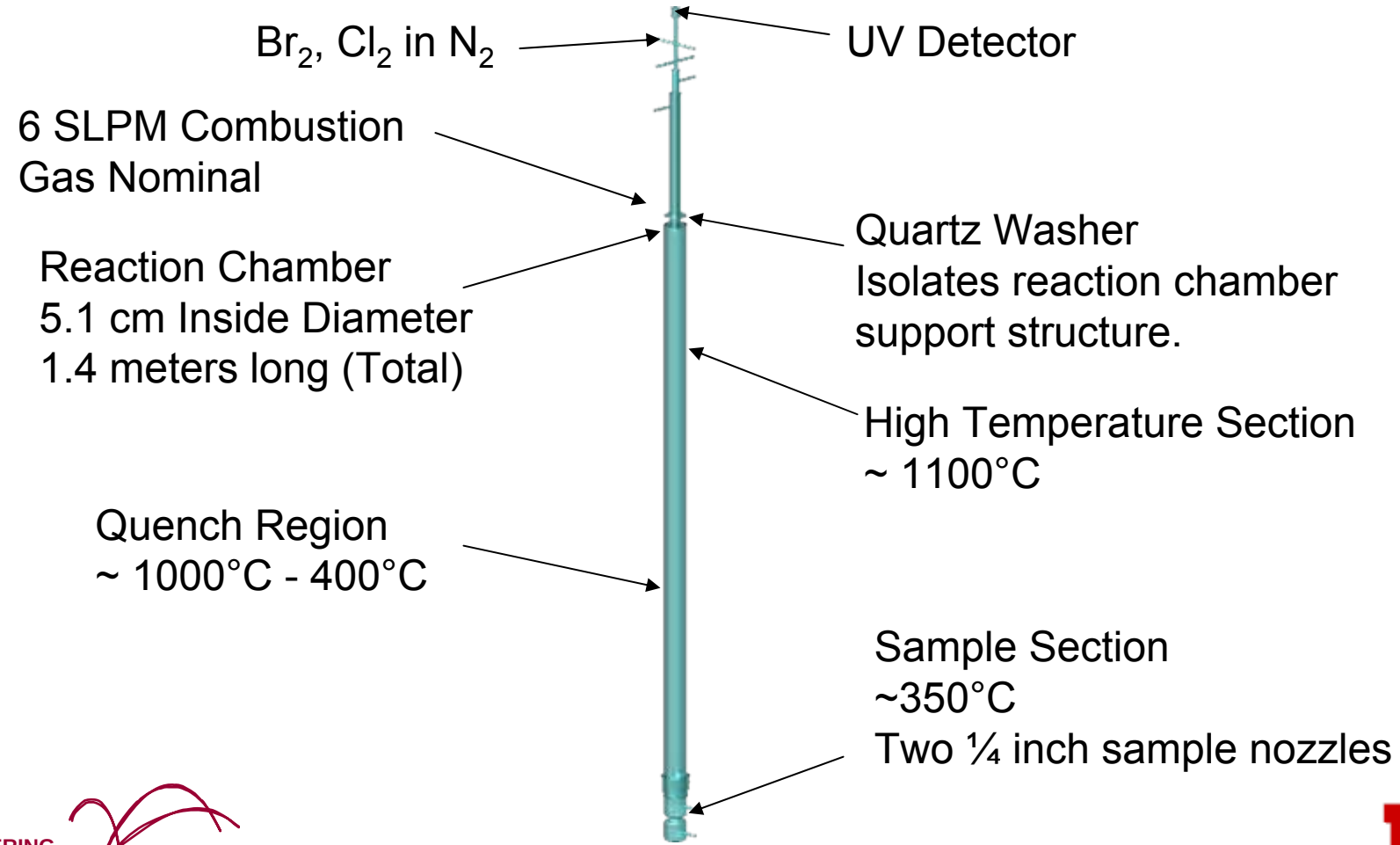
- Predicted homogeneous oxidation by halogens is negligible



- Equivalent coal halogens:
  - 70 ug/g Cl
  - 1, 60, 25 ug/g Br
- Equivalent flue gas halogens (as HX):
  - 5.7 ppmv HCl
  - 0.38, 2.3, 4.6 ppmv HBr
- Cl/Br molar ratios: 150, 2.5, 1.2

Quartz Tubular Reactor

- 300 W (1000 Btu/h), methane-fired



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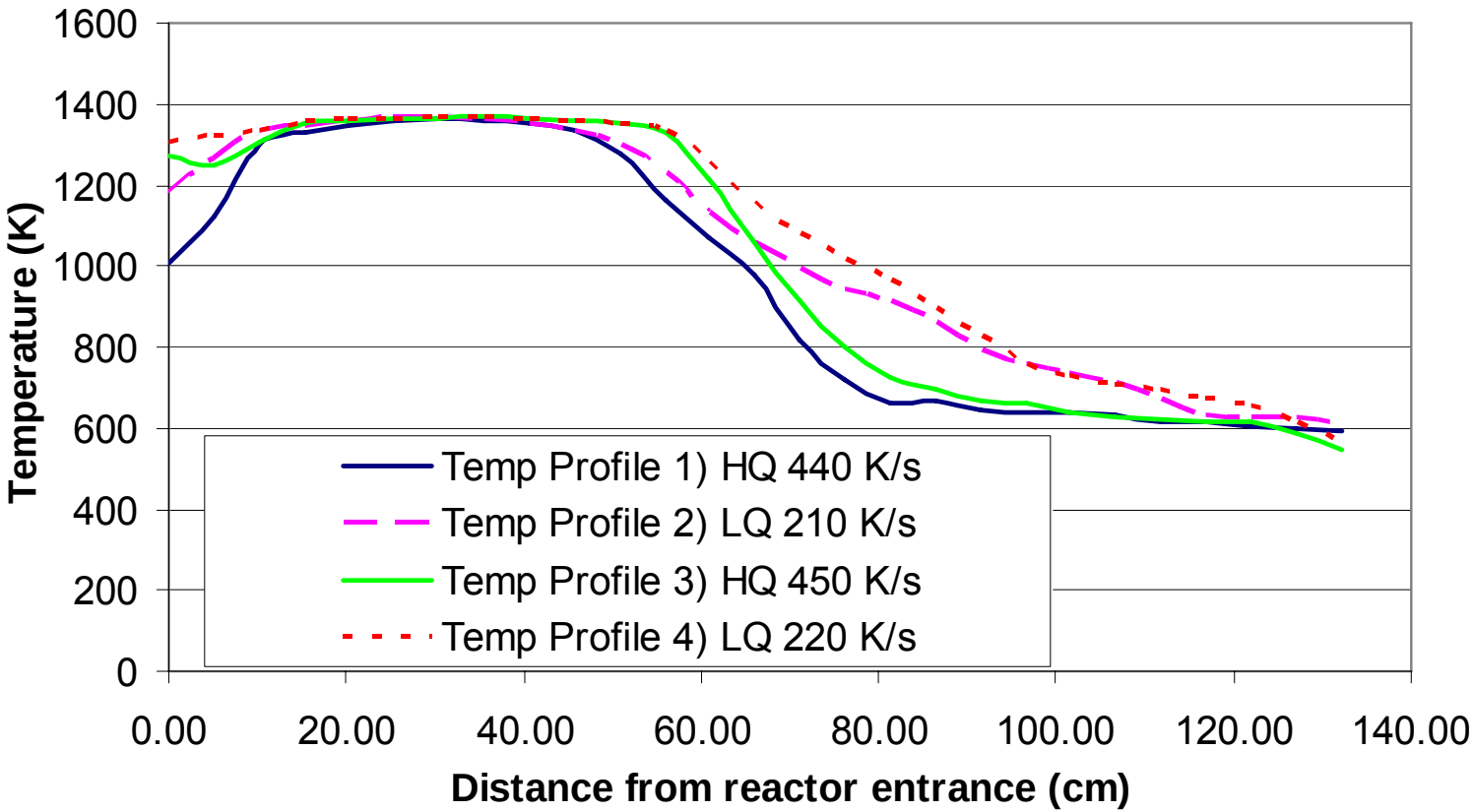
Quartz Tubular Reactor

- Temperature profiles



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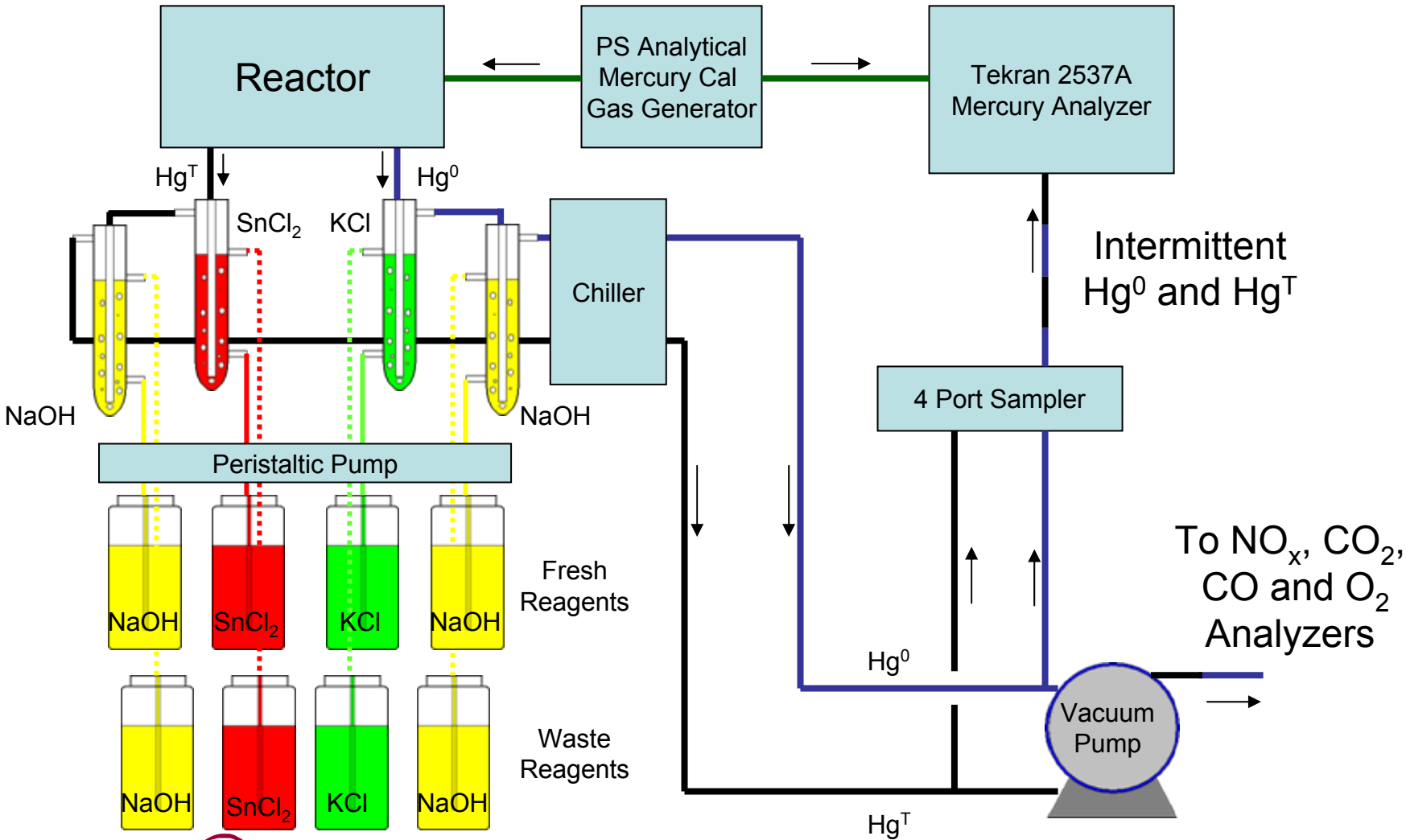
Sample Conditioning System



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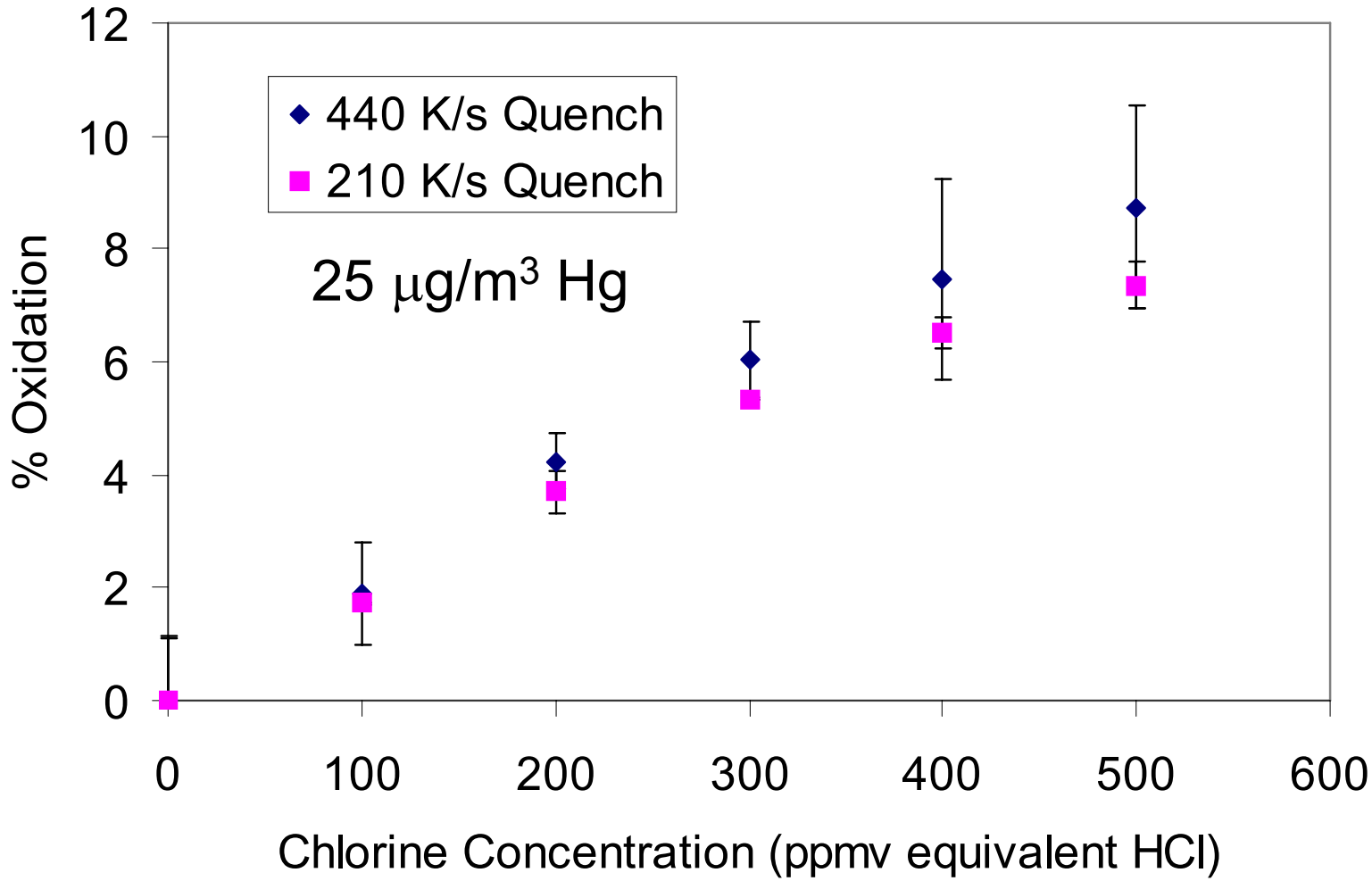
Sample Conditioning System

- Sodium thiosulfate added to KCl impinger to prevent oxidation of Hg^0 by hypochlorous acid.
  - $Cl_2 + H_2O \rightarrow HOCl + HCl$
  - $HOCl + HCl + Hg^0 \rightarrow HgCl_2 + H_2O$
  - $Na_2S_2O_3 + 4\ Cl_2 + 5\ H_2O \rightarrow 2NaHSO_4 + 8\ HCl$
  - $Na_2S_2O_3 + 2\ HCl \rightarrow 2NaCl + H_2O + S + SO_2$

Oxidation by chlorine



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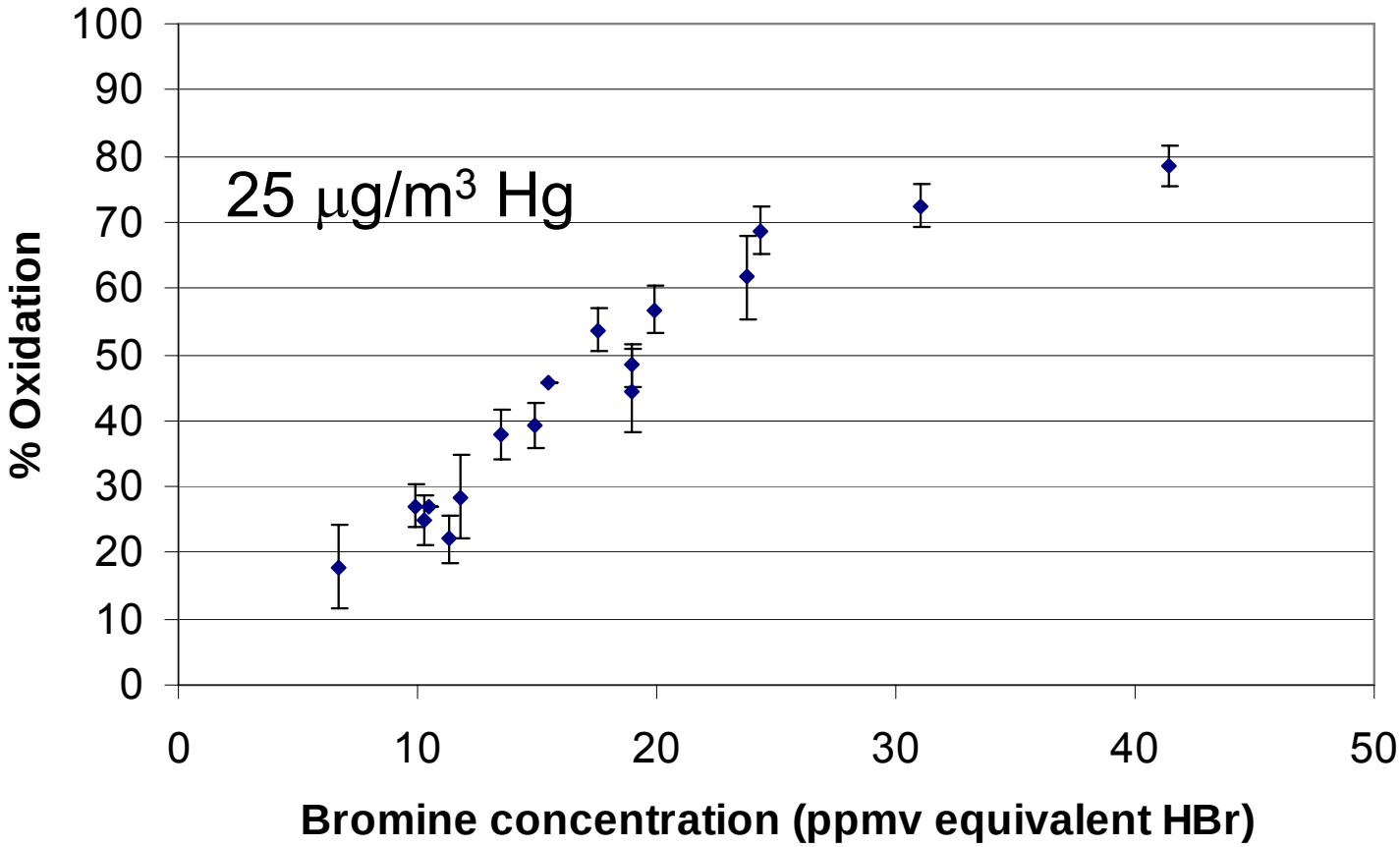
Oxidation by Bromine – Effect of Concentration

HQ (450 K/s), 1.5% O_2 (dry), 30 ppm NO (dry)



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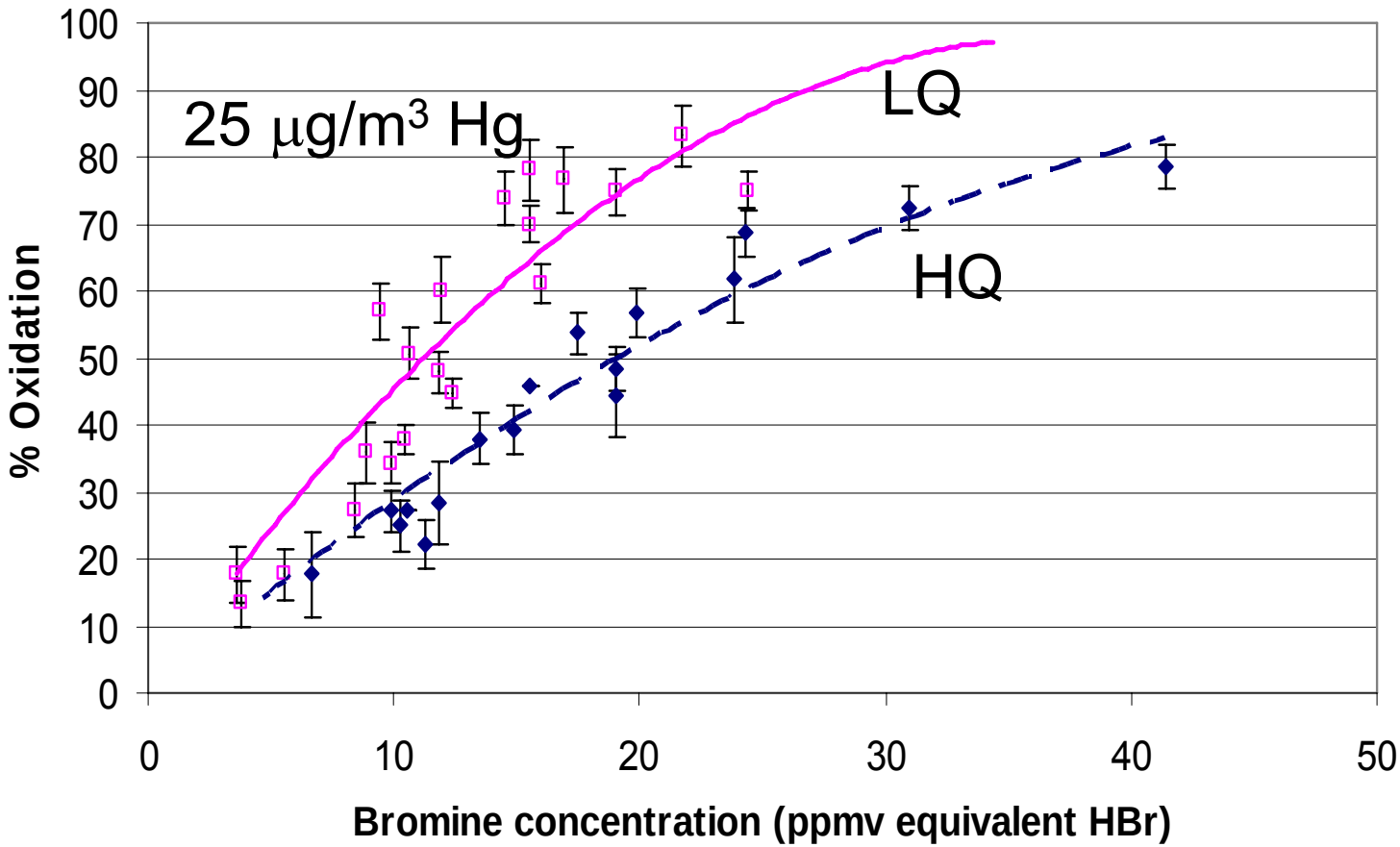
Oxidation by Bromine – Effect of T Profile

LQ (220 K/s), 1.5% O_2 (dry), 30 ppm NO (dry)



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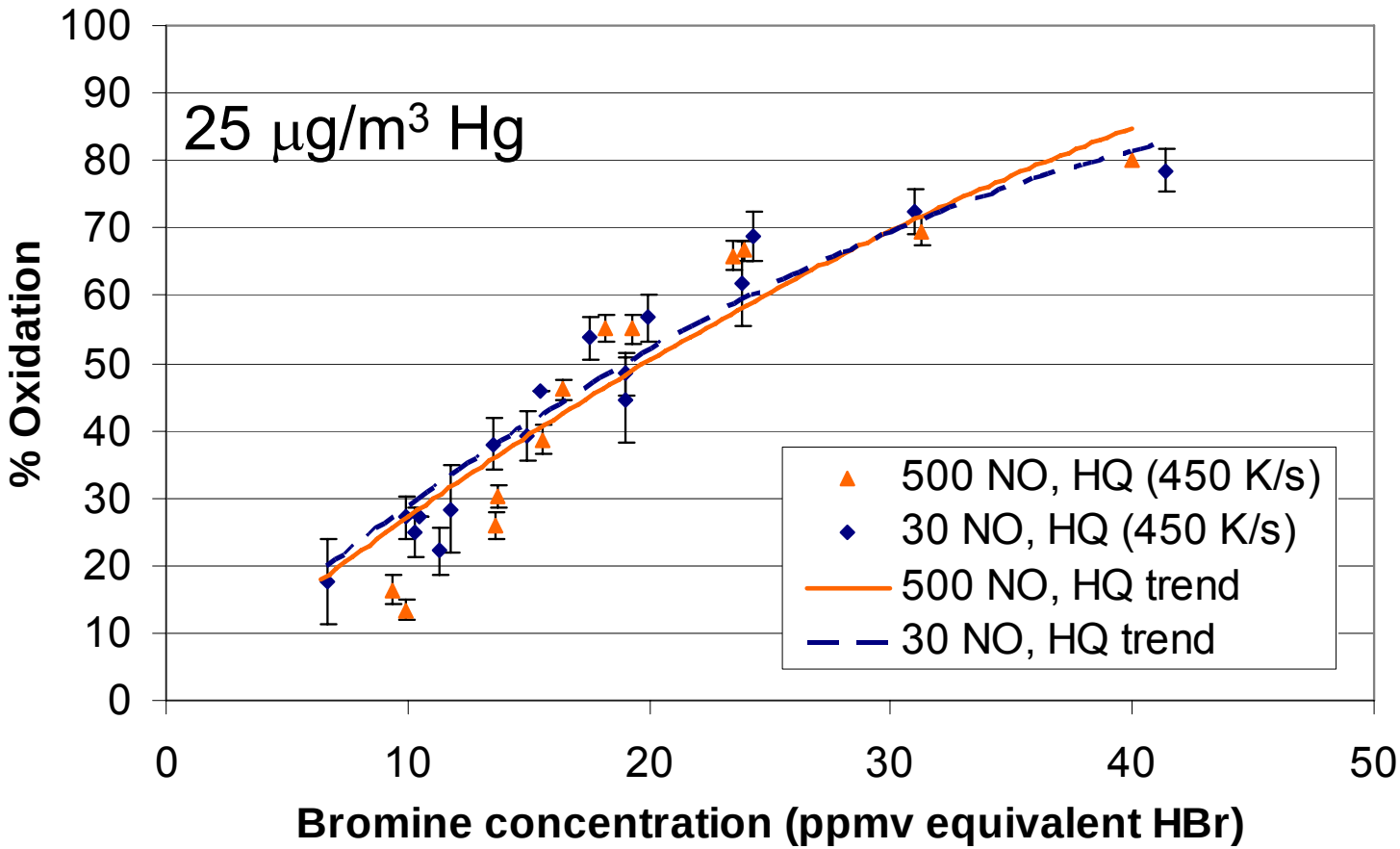
Oxidation by Bromine – Effect of NO

HQ (450 K/s), 1.5% O_2 (dry), 500 ppm NO (dry)



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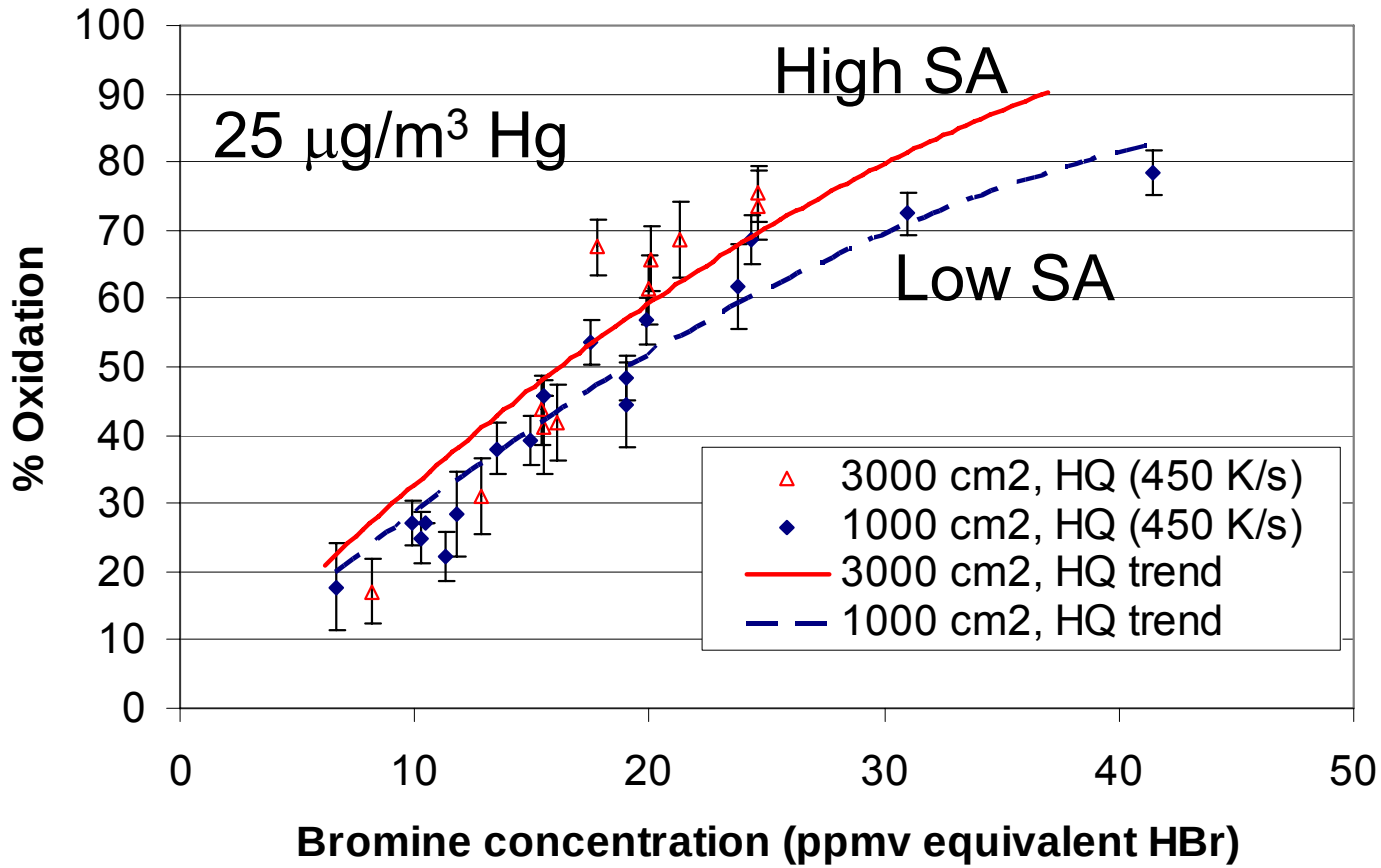
Oxidation by Bromine – Effect of Reactor Surface Area

HQ (450 K/s), 1.5% O_2 (dry), 30 ppm NO (dry), Tube Bundle



Future Work

- Heterogeneous oxidation on carbon
- Modeling – homogeneous and heterogeneous reactions

(1) $Hg^0 + site \rightarrow Hg^0\text{-site}$

(2) $NO_2 + site \rightarrow NO_2\text{-site}$

(3) $HCl + site \rightarrow HCl\text{-site}$

(4) $Hg^o\text{-site} + NO_2\text{-site} + 2HCl\text{-site} \rightarrow HgCl_2\text{-site} + H_2O \uparrow + NO \uparrow + 2\ sites$

(5) $HgCl_2\text{-site} \rightarrow HgCl_2 \uparrow + site$

(6) $SO_2 + site \rightarrow SO_2\text{-site}$

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Conclusions

- From thermodynamics, Br_2 and HCl are dominant species at 300°C.
- $HgCl_2$ and $HgBr_2$ are stable below about 500°C.
- Currently available kinetic models for homogeneous oxidation do not agree with our data.
- Sodium thiosulphate is essential for sample conditioning in absence of SO_2.

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Conclusions

- Homogeneous oxidation by chlorine is about 5% at 300 ppm Cl as HCl.
- Homogeneous oxidation by bromine is about 50% at 20 ppm Br as HBr.
- Homogeneous oxidation by chlorine is insensitive to quench rate while oxidation by bromine increases with lower quench rate.

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Conclusions

- Homogeneous oxidation of mercury by halogens is unaffected by NO and SO_2.
- Extents of oxidation are insensitive to interior, quartz reactor surface area which implies that we are measuring homogeneous oxidation.

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